

Investigation of Ions and Solvent Insertion in Conducting Polymers by ac-Electrogravimetry.

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Introduction. It is now commonly admitted that anions, cations and solvent are both involved during the switching between oxidation states of electroactive polymers. Despite the numerous past studies, there are still many remaining questions regarding the kinetics of the species, ions and solvent, transferred during a redox reaction. In fact, in practical applications, especially in fuel cell technology, electrode performances are governed by the rate determining step at which the charges are exchanged. In many cases ions and solvent transfer at the polymer/solution interface has been found to be slower than electron motion which balance them to reach electroneutrality.

The usual technique used to investigate these charge compensation processes are current and mass responses to a potential scan by means of a potentiostatic arrangement coupled with a quartz crystal microbalance. A new approach is based on the frequency analysis of both current and mass which allows a real dissection of the whole process and the separation of the movements of each species. Ac-electrogravimetry, where the usual impedance is simultaneously measured with the mass/potential transfer function, is proposed.

Here, very thin films where charge transport in the polymer is not limiting were used. The rate limiting step was the ionic transfer at the polymer/electrolyte interface.

Experimental. Measurements were carried out by means of a conventional potentiostatic set-up coupled with a fast quartz crystal microbalance. The impedance and the mass/potential transfer function were simultaneously measured using a four channel frequency analyser (Solartron 1254).

Applications. Figure 1 shows the mass/potential transfer function for a polypyrrole film immersed

in 0.1 M Na₂SO₄ at -0.55 V/SCE. Three loops in the diagram demonstrate the movement of three species during the switching of the polymer between reduced and oxidized states. The continuous line shows the prediction of the model proposed.

Fig. 1 : Mass/potential transfer function measured on polypyrrole in 0.1 M Na₂SO₄ at -0.55 V/SCE. Continuous line shows the model prediction.

Figure 2 presents the derivative of the insertion/expulsion isotherm directly obtained from the mass/potential transfer function.

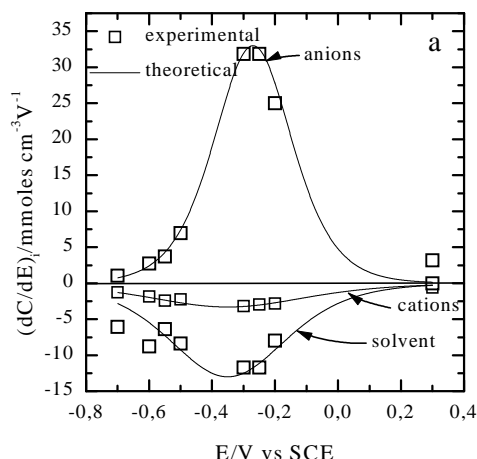


Fig. 2 : Derivatives of the insertion/expulsion isotherm of anions, cations and solvent in 0.25 M NaCl.

Conclusion. Ac-electrogravimetry allows anions, cations, and solvent kinetics to be separated during the exchange occurring during the redox reaction of a conducting polymer. The insertion/expulsion isotherms are determined and the species involved are chemically identified.

References

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